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FURTHER STUDIES ON THE 1,4 ADDITION REACTION OF HEXAFLUOROBUT-2-YNE TO RHODIUM(I)-β-KETOENOLATE RINGS AND RELATED SYSTEMS

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Summary

Hexafluorobut-2-yne reacts with the β-ketoaminato complexes, $Rh(apeo)L_2$ ($L = C_2H_4$; L_2 = cod, nbd) and the β-ketoenolate complexes, $Rh(dbm)(cod)$, $Rh(aan)L_2$, $Rh(dpm)L_2'$, (L_2' = Dhmb, cot) and $Rh(acac)(Me_2C{=}C{=}CMe_2)_2$ to give η^4-hexakistrifluoromethylbenzene complexes of 1,4 addition products of a rhodium(I) β-ketoaminate or -ketoenolate ring system with the acetylene. However, in contrast to these reactions hexafluorobut-2-yne reacts with $Rh(dpm)(C_2H_4)_2$ to give a 1,4 addition product which contains a 1,2,3,4 tetrakis(trifluoromethyl)cyclohexa-1,3-diene ligand.

Hexafluorobut-2-yne, dimethylacetylenedicarboxylate and diethylacetylenedicarboxylate react with $Rh(dpm)(C_2F_4)(L")$ to give the metallacyclopentadiene complexes $Rhdpm(C_4R_4)(L")$, ($L"$ = $AsPh_3$, R = CF_3, CO_2Me or CO_2Et; $L"$ = $SbPh_3$, R = CF_3 or CO_2Et) and it is apparent that triphenylarsine and triphenylstibine ligands inhibit 1,4 addition to the β-ketoenolate ring.†

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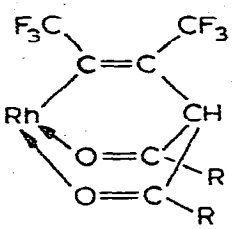
† Abbreviations used in this paper; Dhmb, Dewarhexamethylbenzene; cot, cyclo-octatetraene; cod, 1,5-cyclo-octadiene; nbd, norbornadiene; acac, acetylacetonato; dpm, dipivaloylmethanato; apeo, 4-aminopent-3-ene-2-onato; dbm, dibenzoylmethanato; aan, acetoacetanilido

Introduction

STUDIES on the interaction of hexafluorobut-2-yne with some d^8 rhodium(I) acetylacetonato and dipivaloylmethanato complexes have shown that this highly electrophilic alkyne adds 1,4 to the metalla-β-ketoenolate system to give products containing the bicyclic unit (I).[1-3] Continuing



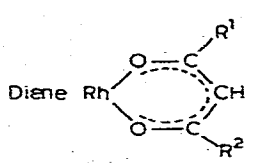
R = Me, CMe_3

(I)

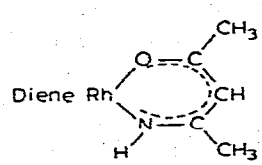
out studies on the reactions of β-ketoenolate systems we have now investigated the action of hexafluorobut-2-yne on some β-ketoaminato complexes and other ring systems and have studied the effect of co-ordinated triphenylarsine and triphenylstibine on the 1,4 addition reaction. Recently it has been shown that a 2,4-pentanediiminato chelate ring of a macrocyclic cobalt(II) complex undergoes similar four-centre reactions with dioxygen, nitriles and alkynes.[4]

Results and Discussion

The interaction of hexafluorobut-2-yne with the β-ketoenolate complexes (IIa), (IIb) and the β-ketoaminato complexes, complexes (III), at room temperature in diethyl ether solution results in

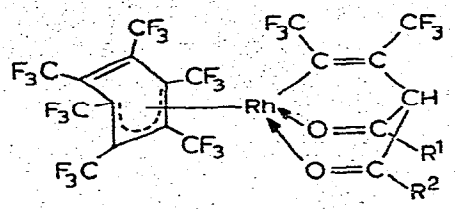


(IIa), $R^1 = R^2 = Ph$; Diene = cod
(IIb), $R^1 = Me$, $R^2 = NHPh$; Diene = cod,nbd

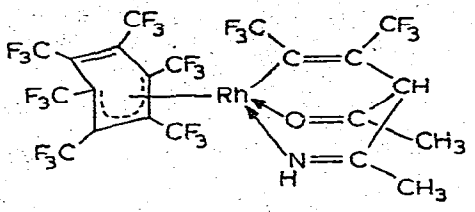


(III), Diene = cod,nbd

the formation of the air-stable yellow crystalline adducts (IVa), (IVb) and (V) respectively. These complexes are formulated as 1,4 addition



(IVa), $R^1 = R^2 = Ph$
(IVb), $R^1 = Me$, $R^2 = NHPh$



(V)

products containing co-ordinated hexakis(trifluoromethyl)benzene on the basis of microanalytical and molecular weight data (Table 1) and their ^{19}F n.m.r. spectra which are similar to that observed for the analogous product obtained with acetylacetonato(cyclo-octa-1,5-diene) rhodium(I).[2] The i.r. spectra of these complexes (Table 3) show bands which can be assigned to ν(C=C) of the vinylic system $RhC(CF_3)=C(CF_3)$ as well as bands attributable to the unco-ordinated double bond of the η^4-$C_6(CF_3)_6$ ligand. In addition the i.r. spectrum of the complex (V) shows a strong band at 1686 cm^{-1} in the region associated with C=O and C=N stretching frequencies and by analogy with our previous studies with β-ketoenolate systems[1-3] we favour a structure for (V) in which both the oxygen and nitrogen atoms of the C=O and C=N groups are co-ordinated to the rhodium which thereby becomes formally five co-ordinate.

The complexes (IVb) and (V) are air-stable and can be readily re-crystallised from common organic solvents, and their stability and ease of formation can be correlated with the presence of the electron donating methyl and anilido substituents. However, the complex (IVa) formed from the dibenzoylmethanato complex was less easily formed and readily decomposed under the reaction conditions. This observation provides further evidence[2] that electron-withdrawing substituents tend to inhibit the 1,4 addition reaction. In the present studies we have observed no difference between the reactions of either the cyclo-octa-1,5-diene complexes or the norbornadiene complexes with hexafluorobut-2-yne. This is similar to the situation observed with the dipivaloyl methanato complexes [Rh(dpm)(nbd)] and [Rh(dpm)(cod)].[2] However, it should be

TABLE 1

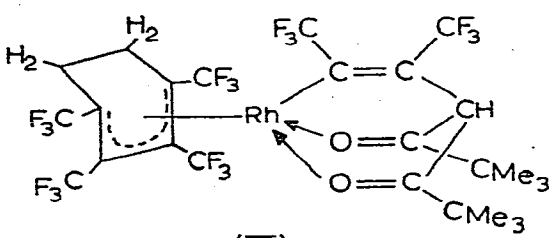
	Compound	Colour	M.p. °C[a]	Analysis (%)[b] C	H	F	N	Mol. wt.
(IVa)	[Rh{dbm.C_4F_6}{η^4-$C_6(CF_3)_6$}][d]	Orange	200 (dec)	33.8 (33.4)	1.20 (1.10)	49.1 (50.9)		
(IVb)	[Rh{aan.C_4F_6}{η^4-$C_6(CF_3)_6$}]	p.yellow	209 (dec)	33.9 (33.7)	1.30 (1.10)	48.7 (49.2)	1.30 (1.10)	856 (928)[c]
(V)	[Rh{apao.C_4F_6}{η^4-$C_6(CF_3)_6$}]	yellow	190 (dec)	30.2 (30.3)	0.90 (0.80)	54.9 (54.8)	1.90 (1.70)	814 (850)[c]
(VI)	[Rh{dpm.C_4F_6}{η^4-$C_6(CF_3)_4H_4$}]	yellow	224 (dec)	34.7 (34.7)	2.10 (2.00)	49.1 (48.8)		794 (934)[c]
(VIIIa)	[Rh(dpm){$C_4(CF_3)_4$}($AsPh_3$)]	p.yellow	215 (dec)	44.2 (44.4)	3.50 (3.70)	24.7 (25.0)		900 (914)[d]
(VIIIb)	[Rh(dpm){$C_4(CF_3)_4$}($SbPh_3$)]	yellow	229 (dec)	46.0 (46.1)	3.30 (3.50)	24.1 (23.7)		
(IXa)	[Rh(dpm){$C_4(CO_2Me)_4$}($AsPh_3$)]	p.yellow	236 (dec)	56.1 (56.4)	5.20 (5.30)			856 (874)[d]
(IXb)	[Rh(dpm){$C_4(CO_2Et)_4$}($AsPh_3$))	p.yellow	210 (dec)	57.1 (57.6)	5.60 (5.20)			910 (934)[d]
(IXc)	[Rh(dpm){$C_4(CO_2Et)_4$}($SbPh_3$)]	p.yellow	208 (dec)	54.9 (55.1)	5.30 (5.10)			960 (982)[d]

[a] Uncorrected [b] Required values in parentheses [c] Determined osmometrically in acetone [d] Determined osmometrically in $CHCl_3$

Abbreviations such as Rh{dbm.C_4F_6} indicate the stoichiometry of the bicyclo system formed by 1,4 addition of hexafluorobut-2-yne to the Rh β-ketoenolate ring.

noted that the reactions of hexafluorobut-2-yne with the acetylacetonato complexes [Rh(acac)(nbd)] and [Rh(acac)(cod)] are different.[2] Thus although hexafluorobut-2-yne affects the displacement of cyclo-octa-1,5-diene from the rhodium, one double band of the diene in the norbornadiene complexes joins with the acetylene and rhodium to form a rhodacyclopentene ring system.

Significant differences have also now been observed in the reactions of hexafluorobut-2-yne with the bis-ethylene complexes [Rh(dpm)$(C_2H_4)_2$], [Rh(apeo)$(C_2H_4)_2$] and [Rh(aan)$(C_2H_4)_2$]. Treatment of the dipivaloylmethanato complex, [Rh(dpm)$(C_2H_4)_2$] with hexafluorobut-2-yne gives a 1,2,3,4-tetrakis (trifluoromethyl)cyclohexa-1,3-diene complex, (VI)

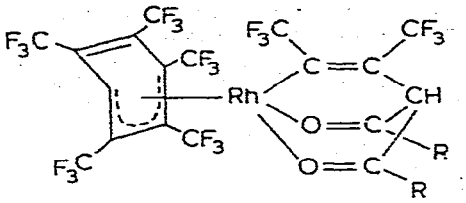


(VI)

analogous to the corresponding complex obtained with [Rh(acac)$(C_2H_4)_2$] and which shows the expected i.r. spectrum and characteristic n.m.r. parameters. In contrast, however, hexafluorobut-2-yne reacts with the 4-aminopent-3-ene-2-onato and acetoacetanilido complexes, [Rh(apeo)$(C_2H_4)_2$] and [Rh(aan)$(C_2H_4)_2$] to give the complexes (V) and IVb) respectively.

Recently it has been shown that a metallocyclopentadiene molecule is a key intermediate in the cyclotrimerisation of two molecules of acetylene and one molecule of olefin to form cyclohexa-1,3-diene derivatives.[5] A similar mechanism may operate in the formation of (VI) although an alternative mechanism involving attack of hexafluorobut-2-yne upon a rhodacyclopentene ring system could be involved in the reaction.[6] Attempts to incorporate Dewarhexamethylbenzene, cyclo-octatetraene or tetramethylallene into ring systems with hexafluorobut-2-yne were not successful. Thus reaction of [Rh(dpm)(Ohmb)] or [Rh(dpm)(cot)] with hexafluorobut-2-yne

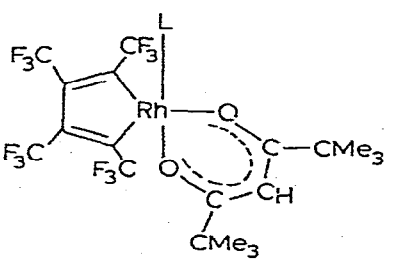
results in complete displacement of the diene to give (VIIa) identical to the complex



(VIIa), R = CMe_3
(VIIb), R = Me

previously obtained from hexafluorobut-2-yne and [Rh(dpm)(cod)].[2] Similarly reaction of hexafluorobut-2-yne with [Rh(acac)($Me_2C{=}C{=}CMe_2$)$_2$] gives (VIIb) also identical to the complex previously obtained using [Rh(acac)(cod)].

In an attempt to study the incorporation of tetrafluoroethylene into a ring system and also to study the effect of ligands other than dienes on the 1,4 addition reaction the reactions of hexafluorobut-2-yne with the complexes [Rh(dpm)(C_2F_4)(L)], (L = $AsPh_3$ or $SbPh_3$) were investigated. Treatment of [Rh(dpm)(C_2F_4)($AsPh_3$)] with hexafluorobut-2-yne in diethyl-ether solution at room temperature gives a light yellow crystalline complex formulated as (VIIIa). The i.r. spectrum of (VIIIa) shows bands



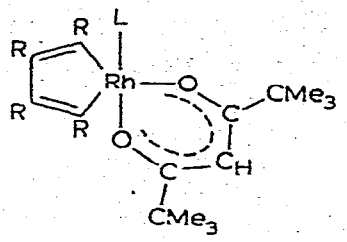
(VIIIa), L = $AsPh_3$
(VIIIb), L = $SbPh_3$

at 1566, 1548 and 1520 cm^{-1} typical of a normal oxygen bonded β-ketoenolate system. In addition there are two bands at 1582 and 1538 cm^{-1} of medium intensity which are characteristic of a tetrakis(trifluoromethyl)rhoda-cyclopentadiene moiety, and in particular there are two sharp bands at 657 and 648 cm^{-1} which suggest the presence of a five-co-ordinate rhoda-

cyclopentadiene complex.[7] The triphenylstibine complex (VIIIb) was prepared in an analogous manner and has similar absorptions in its i.r. spectrum, (Table 3).

At room temperature the ^{19}F n.m.r. spectrum of an acetone solution of (VIIIa) exhibited two broad signals of equal intensity centred at -11.48 and -6.16 p.p.m. relative to benzotrifluoride. The ^{1}H n.m.r. spectrum contains well resolved absorptions at 2.96 (br, 15H), 3.85 (s, 1H) and 8.80τ (s, 18H). On recording the ^{1}H n.m.r. spectrum at -65° (CH_2Cl_2 solution) the tertiary butyl signal splits into two singlets of equal intensity at 8.73 and 8.92τ, but the ^{19}F n.m.r. spectrum at this temperature remains unchanged. Equivalence of the tertiary butyl groups can be achieved by a non-dissociative mechanism involving a Berry pseudo-rotation[8] or related process.[9-11] Alternatively a dissociative mechanism could operate which could involve cleavage of a rhodium-oxygen bond[12] of the acetylacetonato system or loss of the triphenylarsine ligand. The observation that the coalescence temperature of the t-butyl signals in the ^{1}H n.m.r. spectra of (VIIIa) occurs at -51° in CH_2Cl_2 and at -5° in D^6 acetone solution is more consistent with a dissociative mechanism since it would be expected that the intermediates involved in such a process would be stabilised to different extents in solvents of different polarity. Further since added triphenylarsine has no effect on the coalescent temperature the exchange process probably involves cleavage of the acetylacetonato ring. By analogy with the structure[13] of $[RhCl\{C_4(CF_3)_4\}(SbPh_3)_2]$ it is possible that in the solid state (VIIIa) may also have a structure based on a trigonal bipyramid. The triphenylstibine complex (VIIIb) is not sufficiently soluble for n.m.r. studies.

Complexes (IXa - IXc) analogous to (VIIIa) may also be obtained by treating $[Rh(dpm)(C_2F_4)L]$, with either dimethyl- or diethylacetylenedicarboxylate although in the reaction of $[Rh(dpm)(C_2F_4)(SbPh_3)]$ with $MeO_2CC{\equiv}CCO_2Me$ polymerisation of the acetylene to hexakis(carbomethoxy) benzene occurred and only a brown intractable oil could be obtained from the residue. The ^{1}H n.m.r. spectra of the complexes (IXa - IXc), (Table 2)



(IXa) L = $AsPh_3$; R = CO_2Me
(IXb) L = $AsPh_3$; R = CO_2Et
(IXc) L = $SbPh_3$; R = CO_2Et

are consistent with a five co-ordinate metallacyclopentadiene structure and show that they are fluxional at room temperature. However, in contrast to (VIIIa) the tertiary butyl signals show only slight broadening upon cooling to -90^{o}.

It is apparent from these studies that coordination of triphenylarsine or triphenylstibine inhibits 1,4 addition of electrophilic acetylenes to the β-ketoenolate ring system. Instead an oxidative addition reaction involving two molecules of the acetylene takes place at the rhodium to generate a rhodacyclopentadiene ring system. The subsequent increased formal positive charge at the rhodium will therefore inhibit addition to the β-ketoenolate ring system. Since dienes are known to inhibit oxidative addition at rhodium(I),[14] this pathway is less likely to be observed in complexes of the type [Rh(β-ketoenolate)(diene)] and 1,4 addition can therefore occur.

Experimental

Analytical data and melting points for all new complexes are given in Table 1. ^{1}H (Table 2) and ^{19}F n.m.r. spectra were obtained using Varian Associates T60 and DA60 spectrometers respectively. The ^{19}F n.m.r. spectra were measured relative to benzotrifluoride as internal standard and were recorded at 56.4 MHz.

TABLE 2

^{1}H data for the complexes (IV)-(IX)

	Solvent[c]	3-CH[d]	OR	Bu^t [g]	Me	Other
(IVa)	A					2.43(m,10H)
(IVb)	A	4.10			7.20(s,3H)	2.74(m,5H)
(V)	A	4.30			7.24(s,3H),7.26(s,3H)	3.96(s,1H)
(VI)	A	3.40		8.74		7.76(d,2H,J_{HH}8Hz) 9.06(d,2H,J_{HH}8Hz)
(VIIIa)	B	3.85		8.80		2.96(m,15H)
(IXa)	B	4.88	6.46(s,6H);6.61(s,6H)	9.15		2.36(m,15H)
(IXb)	B	5.16	6.16(q,4H), 6.31(q,4H)[e] 9.01(t,6H), 9.10(t,6H)	9.21		2.82(m,15H)
(IXc)	B	4.61	6.13(q,4H), 6.30(q,4H)[f] 8.98 (t,6H), 9.12(t,6H)	9.22		2.80(m,15H)

[a] All chemical shifts quoted in τ. [b] Measured in acetone and reported as p.p.m. relative to internal benzotrifluoride. [c] A is D^6-acetone, B is $CDCl_3$. [d] All singlets, rel. int. [e] J_{HH} = 7.4Hz. [f] J_{HH} = 7.3Hz. [g] All singlets, rel. int. 18H.

TABLE 3

Selected i.r. absorptions for the complexes (IV)-(IX)

	ν(C=O)	ν(C=C)	ν(dpm)	ν(CO_2R)
[Rh(dbm.C_4F_6)(η^4-$C_6(CF_3)_6$)]	1635	1595,1575		
[Rh(aan.C_4F_6)(η^4-$C_6(CF_3)_6$)]	1684	1639, 1601		
[Rh(apao.C_4F_6)(η^4-$C_6(CF_3)_6$)]	1686	1638, 1603		
[Rh(dpm.C_4F_6)(η^4-$C_6(CF_3)_6H_4$)]	1671	1579		
[Rh(dpm.C_4F_6)(η^4-$C_6(CF_3)_6$)]	1660	1640, 1580		
[Rh(acac.C_4F_6)(η^4-$C_6(CF_3)_6$)]	1694, 1662	1642, 1600		
[Rh(dpm)($C_4(CF_3)_4$)($AsPh_3$)]		1582, 1538	1566, 1548, 1520	
[Rh(dpm)($C_4(CF_3)_4$)($SbPh_3$)]		1583, 1534	1564, 1550, 1502	
[Rh(dpm)($C_4(CO_2Me)_4$)($AsPh_3$)]		1583, 1536	1564, 1550, 1512	1716, 1703, 1686
[Rh(dpm)($C_4(CO_2Et)_4$)($AsPh_3$)]		1582, 1532	1563, 1552, 1508	1727, 1702
[Rh(dpm)($C_4(CO_2Et)_4$)($SbPh_3$)]		1581, 1537	1561, 1548, 1506	1720, 1701

The complexes [Rh(acac)(Me$_2$C=C=CMe$_2$)$_2$],[15] [Rh(dpm)(C$_2$F$_4$)(AsPh$_3$)][16] and [Rh(dpm)(C$_2$F$_4$)(SbPh$_3$)][16] were prepared as described in the literature. The complexes [Rh(apeo)(cod)],[Rh(apeo)(nbd)],[Rh(apeo)(C$_2$H$_4$)$_2$],[17,18] [Rh(dbm)(cod)], [Rh(aan)(cod)],[Rh(aan)(nbd)],[Rh(aan)(C$_2$H$_4$)$_2$],[Rh(dpm)(cot)], [Rh(dpm)(Ohmb)] and [Rh(dpm)(C$_2$H$_4$)$_2$] were prepared by the following general method. An excess of the appropriate β-diketone or β-ketoamine was added to a suspension of the corresponding chloride dimer of the type [RhCl(olefin)$_2$]$_2$ in diethylether containing a little aqueous potassium hydroxide. After stirring for 30 min., the ether layer was extracted and the product obtained by crystallisation from diethyl ether-methanol mixtures. All the compounds made in this way gave the expected ^{1}H n.m.r. and i.r. spectral data and their purity was confirmed by elemental analysis, [Rh(apeo)(cod)], (82%), m.p. 165° (Found: C,50.4; H,6.5. $C_{13}H_{20}ONRh$ requires C,30.5;H,6.5%). [Rh(apeo)(nbd)], (79%), m.p. 141° (Found: C,51.3; H,5.5, $C_{12}H_{16}ONRh$ requires C,51.2; H,5.3%). [Rh(apeo)(C$_2$H$_4$)$_2$], (81%), m.p. 97° (Found: C,42.1; H,6.2, $C_9H_{12}ONRh$ requires C,42.0; H,6.2%). [Rh(dbm)(cod)], (67%), m.p. 182° (Found: C,63.6; H,5.5, $C_{23}H_{23}O_2Rh$ requires C,63.5; H,5.4%). [Rh(aan)(cod)], (57%), m.p. 191° (Found: C,55.7; H,5.8. $C_{17}H_{22}O_2NRh$ requires C,55.8; H,5.7%). [Rh(aan)(nbd)], (43%), m.p. 160° (dec) (Found: C,57.4; H,5.10. $C_{17}H_{18}O_2NRh$ requires C,57.4; H,5.05%). [Rh(aan)(C$_2$H$_4$)$_2$], (77%), m.p. 156° (dec) (Found: C,52.2; H,5.40. $C_{14}H_{18}O_2NRh$ requires C,52.5; H,5.65%). [Rh(dpm)(cot)], (78%), m.p. 101° (Found: C,58.6; H,6.0. $C_{19}H_{27}O_2Rh$ requires C,58.5; H,6.6%). [Rh(dpm)(Ohmb)], (84%), m.p. 110° (Found: C,62.5; H,6.7. $C_{23}H_{37}O_2Rh$ requires C,62.7; H,6.9%). [Rh(dpm)(C$_2$H$_4$)$_2$], (91%), m.p. 98° (Found: C,52.5; H,7.8. $C_{15}H_{27}O_2Rh$ requires C,52.6; H,7.9%).

(a) Preparation of [Rh(dbm.C$_4$F$_6$)(η^4-C$_6$(CF$_3$)$_6$)]

An excess of hexafluorobut-2-yne (1.0 ml) was condensed (-196°) onto a solution of dibenzoylmethanato(cyclo-octa-1,5-diene) rhodium(I) (0.40 g, 0.92 mmol) in diethyl ether contained in a Carius tube (150 ml).

After shaking at 45° for 10 minutes, the tube was opened, the orange precipitate filtered off, and washed with light petroleum to yield complex (IVa), [Rh{dbm.C_4F_6}{η^4-$C_6(CF_3)_6$}] which could not be purified further without serious decomposition. (0.17 g, 19%). ν_{max}; 1635 s, 1593 s, 1575 s, 1292 s, 1256 s, 1217 s, 1190 s, 1152 s, 1074 s, 1008 w, 994 w, 870 w, 837 w, 786 w, 764 w, 740 s, 718 w, 710 w, cm^{-1}.

(b) Preparation of [Rh{aan.C_4F_6}{η^4-$C_6(CF_3)_6$}].

An excess of hexafluorobut-2-yne (1.0 ml) was condensed (-196°) onto a solution of acetoacetanilido(cyclo-octa-1,5-diene) rhodium(I) (0.60 g, 1.53 mmol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 18 hours, the tube was opened and volatile material removed. Slow evaporation of the solution to about 2 ml. gave pale yellow crystals of complex (IVb), [Rh{aan.C_4F_6}{η^4-$C_6(CF_3)_6$}], (0.55 g, 39%). ν_{max}; 3840 m, 1684 s, 1639 s, 1601 s, 1541 s, 1310 m, 1290 s, 1259 s, 1229 s, 1200 s, 1157 s, 1076 s, 942 w, 910 w, 873 w, 840 w, 812 w, 882 w, 757 s, 745 s, 720 m, cm^{-1}.

Similarly [Rh(aan)(nbd)] and [Rh(aan)$(C_2H_4)_2$] react with hexafluorobut-2-yne to give [Rh{aan.C_4F_6}{η^4-$C_6(CF_3)_6$}] in yields of 52 and 38% respectively, the product being identified in each case by its characteristic i.r. and ^{19}F n.m.r. spectra.

(c) Preparation of [Rh{apeo.C_4F_6}{η^4-$C_6(CF_3)_6$}].

An excess of hexafluorobut-2-yne (1.0 ml) was condensed (-196°) onto a solution of 4-aminopent-3-ene-2-onato(cyclo-octa-1,5-diene) rhodium(I) (0.40 g, 1.30 mmol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 2 days the tube was opened and volatile material removed. Slow evaporation of the solution to about 2 ml gave bright yellow crystals of complex (V), [Rh{apeo.C_4F_6}{η^4-$C_6(CF_3)_6$}], (0.81 g, 78%). ν_{max}; 1671 s, 1579 m,

1300 s, 1276 s, 1238 s, 1193 s, 1160 s, 1117 s, 1060 s, 1058 s, 1014 s, 948 m, 863 m, 810 m, 757 m, 742 m, 716 m, cm^{-1}.

(e) Reaction of [Rh(dpm)(Dhmb)] with hexafluorobut-2-yne.

An excess of hexafluorobut-2-yne (1.0 ml) was condensed (-196°) onto a solution of dipivaloylmethanato(hexamethylDewarbenzene)rhodium(I) (0.50 g, 1.11 mmol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 24 hours the tube was opened and volatile materials removed. Slow evaporation of the solution to about 2 ml gave bright yellow crystals of complex (VIIa), $[Rh\{dpm.C_4F_6\}\{\eta^4\text{-}C_6(CF_3)_6\}]$ (0.42 g, 39%), which was identified by its i.r. and ^{19}F n.m.r. spectra.[2]

(f) Reaction of [Rh(dpm)(cot)] with hexafluorobut-2-yne.

An excess of hexafluorobut-2-yne (1.0 ml) was condensed (-196°) onto a solution of dipivaloylmethanato(cyclo-octatetraene)rhodium(I) (0.50 g, 1.28 mmol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 12 hours the tube was opened and volatile material removed. Slow evaporation of the solution to about 2 ml gave bright yellow crystals of complex (VIIa), $[Rh\{dpm.C_4F_6\}\{\eta^4\text{-}C_6(CF_3)_6\}]$, (1.01 g, 84%), which was identified by its i.r. and ^{19}F n.m.r. spectra.[2]

(g) Reaction of $[Rh(acac)(Me_2C{=}C{=}CMe_2)_2]$ with hexafluorobut-2-yne.

An excess of hexafluorobut-2-yne (1.0 ml) was condensed (-196°) onto a solution of acetylacetonatobis(tetramethylallene)rhodium(I) (0.40 g, 1.02 m mol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 4 hours the tube was opened and volatile material removed. Slow evaporation of the solution to about

2 ml. gave yellow crystals of complex (VIIb) [Rh{acac.C_4F_6}{η^4-$C_6(CF_3)_6$}], (0.38 g, 44%), which was identified by its i.r. and ^{19}F n.m.r. spectra.[2]

(h) Reaction of [Rh(dpm)(C_2F_4)($AsPh_3$] with hexafluorobut-2-yne.

An excess of hexafluorobut-2-yne (1.0 ml) was condensed (-196°) onto a solution of dipivaloylmethanato(triphenylarsine)(tetrafluoroethylene) rhodium(I) (0.50 g, 0.77 m mol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 24 hours the tube was opened, volatile material removed and the solution evaporated to dryness. Recrystallisation of the residues from diethyl ether/ethanol gave yellow crystals of complex (VIIIa) [Rh{$C_4(CF_3)_4$}(dpm)($AsPh_3$)], (0.67 g, 88%). Infra-red; 1582 s, 1566 s, 1548 sh, 1538 s, 1520 sh, 1417 s, 1338 s, 1249 s, 1209 s, 1197 s, 1164 s, 1140 s, 1105 s, 1076 s, 879 m, 790 m, 739 s, 691 s, 657 m, 648 m, cm^{-1}.

(i) Reaction of [Rh(dpm)(C_2F_4)($SbPh_3$)] with hexafluorobut-2-yne.

An excess of hexafluorobut-2-yne (1.0 ml) was condensed (-196°) onto a solution of dipivaloylmethanato(triphenylstibine)(tetrafluoroethylene)rhodium(I) (0.50 g, 0.68 m mol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 18 hours the yellow precipitate which had formed was then filtered off and washed with diethyl ether to give yellow microcrystals of complex (VIIIb), [Rh{$C_4(CF_3)_4$}(dpm)($SbPh_3$)], (0.49 g, 73%).
ν_{max}: 1583 s, 1564 s, 1550 m, 1534 s, 1502 s, 1394 s, 1339 s, 1224 s, 1197 s, 1176 s, 1164 s, 1130 s, 1112 s, 1074 m, 876 m, 792 m, 736 s, 698 s, 656 m, 649 m, cm^{-1}.

(j)
Reaction of [Rh(dpm)(C_2F_4)($AsPh_3$)] with dimethylacetylenedicarboxylate.

An excess of dimethylacetylenedicarboxylate (0.50 ml) was added

to a solution of dipivaloylmethanato(triphenylarsine)(tetrafluoroethylene)rhodium(I) (0.50 g, 0.77 m mol) in diethyl ether and the mixture stirred for 30 minutes. The precipitate which had formed was then collected and recrystallised from dichloromethane/$(C_2H_5)_2O$ to give pale yellow crystals of complex (IXa), $[Rh\{C_4(CO_2CH_3)_4\}(dpm)(AsPh_3)]$, (0.51 g, 81%).

ν_{max}: 1716 s, 1703 s, 1686 s, 1583 m, 1564 m, 1550 sh, 1536 m, 1512 w, 1416 s, 1324 m, 1258 s, 1204 s, 1190 s, 1162 s, 1133 m, 1085 m, 1026 m, 988 m, 937 m, 878 m, 786 m, 757 m, 742 s, 736 s, 697 s, 690 s, cm^{-1}.

(k) Reaction of $[Rh(dpm)(C_2F_4)(AsPh_3)]$ with diethylacetylenedicarboxylate.

An excess of diethylacetylenedicarboxylate (0.50 ml) was added to a solution of dipivaloylmethanato(triphenylarsine)(tetrafluoroethylene)rhodium(I) (0.50 g, 0.77 mmol) in diethyl ether and the mixture stirred for 30 minutes. The precipitate which had formed was then collected and recrystallised from dichloromethane/$(C_2H_5)_2O$ to give pale yellow crystals of complex (IXb), $Rh\{C_4(CO_2C_2H_5)_4\}(dpm)(AsPh_3)]$, (0.52 g, 78%).

ν_{max}: 1727 s, 1702 s, 1582 s, 1563 s, 1552 sh, 1532 s, 1508 s, 1442 s, 1410 s, 1399 s, 1341 s, 1258 s, 1216 s, 1190 s, 1132 s, 1117 s, 1064 s, 1042 s, 1024 s, 876 m, 857 s, 784 s, 754 s, 741 s, 698 s, cm^{-1}.

(l) Reaction of $[Rh(dpm)(C_2F_4)(SbPh_3)]$ with dimethylacetylenedicarboxylate.

An excess of dimethylacetylenedicarboxylate (0.50 ml) was added to a solution of dipivaloylmethanato(triphenylstibine)(tetra fluoroethylene)rhodium(I) (0.50 g, 0.68 m mol) in diethyl ether and the mixture stirred for 30 minutes. Concentration of the solution and addition of light petroleum (40-60°) gave white crystals of $C_6(CO_2Me)_6$

which was identified by its m.p. and i.r. spectrum. Attempts to obtain a crystalline product from the residues resulted in only a brown intractable oil being produced.

(m) Reaction of [Rh(dpm)(C_2F_4)($SbPh_3$)] with diethylacetylenedicarboxylate.

An excess of diethylacetylenedicarboxylate (0.50 ml) was added to a solution of dipivaloylmethanato(triphenylstibine)(tetra fluoroethylene)rhodium(I) (0.50 g, 0.68 m mol) in diethyl ether and the the mixture stirred for 30 minutes. The precipitate which had formed was then collected and recrystallised from dichloromethanediethyl ether to give pale yellow crystals of complex (IXc), [Rh{$C_4(CO_2Et)_4$}(dpm)($SbPh_3$)], (0.54 g, 81%).

ν_{max}: 1720s, 1701 s, 1581 s, 1561 s, 1548 sh, 1537 s, 1506 w, 1280 s, 1271 s, 1220 s, 1176 s, 1120 s, 1070 s, 1024 m, 969 m, 784 s, 730 s, 724 s, 719 s, 697 s, 686 s, cm^{-1}.

^{19}F n.m.r. spectra - Spectra were measured in acetone solution relative to internal benzotrifluoride.

[Rh(dbm.C_4F_6)(η^4-$C_6(CF_3)_6$)] : -11.70(br, 9F), -9.85 (br, 6F), -5.55 (br, 6F), -4.10 (q,3F,J_{FF} 15.5 Hz).

[Rh(aan.C_4F_6)(η^4- $C_6(CF_3)_6$)] : -11.90 (br, 9F), -10.40 (br, 3F), -9.44 (br, 3F), -5.70 (br, 6F), -3.78 (q,3F,J_{FF} 15.8 Hz).

[Rh(apeo.C_4F_6)(η^4-$C_6(CF_3)_6$)] : -13.45 (br, 9F), -10.85 (br, 3F), -7.40 (br, 6F), -4.73 (br, 3F), -3.16 (q,3F,J_{FF} 15.8 Hz).

[Rh(dpm.C_4F_6)(η^4-$C_6(CF_3)_4H_4$)] : -10.29 (br, 3F), -8.25 (br, 6F), -6.55 (q,3F,J_{FF} 15.7 Hz), -3.24 (br, 6F).

[Rh(dpm){$C_4(CF_3)_4$}($AsPh_3$)] : -11.48 (br, 6F), -6.16 (br, 6F).

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References

1. D. M. Barlex, J. A. Evans, R. D. W. Kemmitt and D. R. Russell, Chem. Commun., (1971) 331.

2. D. M. Barlex, A. C. Jarvis, R. D. W. Kemmitt and B. Y. Kimura, J. Chem. Soc. Dalton Trans., (1972) 2549.

3. J. A. Evans, R. D. W. Kemmitt, B. Y. Kimura and D. R. Russell, J. Chem. Soc. Chem. Commun., (1972) 509.

4. M. C. Weiss and V. L. Goedken, J. Amer. Chem. Soc., 98 (1976) 3389.

5. H. Suzuki, K. Itoh, Y. Ishii, K. Simon and J. A. Ibers, J. Amer. Chem. Soc., 98 (1976) 8494.

6. Y. Wakatsuki, K. Aoti and H. Yamazaki, J. Amer. Chem. Soc., 1974, 96, 5284.

7. J. T. Maque, M. O. Nutt and E. H. Gause, J. Chem. Soc. Dalton Trans., (1973) 2578.

8. R. S. Berry, J. Chem. Phys., 32 (1960) 933.

9. I. Ugi and F. Ramirez, Chem. Brit., 8 (1972) 198.

10. I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie and F. Ramirez, Accounts Chem. Res., 4 (1971) 288.

11. F. Ramirez, S. Pfohl, E. A. Tsolis, J. F. Pilot, C. P. Smith, I. Ugi, D. Marquarding, P. Gillespie and P. Hoffman, Phosphorus, 1 (197) 1.

12. J. L. Fortman and R. E. Sievers, Coordination Chem. Rev., 6 (1971) 331.

13. J. T. Mague, Inorg. Chem., 9 (1970) 1610.

14. M. A. Bennett, Advances Organometal. Chem., 4 (1966) 353.

15. P. Racanelli, G. Pantini, A. Immirzi, G. Allegra and L. Porri, Chem. Commun., (1969) 361.

16. A. C. Jarvis and R. D. W. Kemmitt, J. Organometallic Chem., 81 (1974) 415.

17. K. Bouchal, J. Kriz and F. Hrabak, Collect. Czech. Chem. Commun., 39 (1974) 439.

18. J. Kriz and K. Bouchal, J. Organometallic Chem., 64 (1974) 255.